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In re Application of: Jun Konishi, Atsushi Sugawara and Yutaka Mitsunaga

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For: Chlorinated Polyolefins and Process for Their Production

VERIFIED TRANSLATION CERTIFICATEHonorable Commissioner of Patents and Trademarks  
Washington, D.C. 20231

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The undersigned, of the below address, hereby verifies that I well know both the English and Japanese languages, and that the attached is a full, true literal and faithful translation into the English language of the 10 page Japanese language application which I am now advised carries U.S. Serial No. 60/412,793 effectively deposited in the United States Patent and Trademark Office on September 24, 2002.

The undersigned declares further that all statements made herein on personal knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 12th day of September, 2003

Translator's Signature:

Name: Tsuguo Yoshida  
Address: c/o A. AOKI, ISHIDA & ASSOCIATES,  
3-5-1, Toranomon, Minato-ku,  
Tokyo 105-8423, Japan

[NAME OF DOCUMENT]

Specification

[TITLE OF INVENTION]

Chlorinated Polyolefins and  
Process for Their Production

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a process for production of chlorinated polyolefins which are suitable as thermoplastic elastomers with excellent low-temperature rubber elasticity and compression set.

[0002]

[Prior Art]

Chlorinated polyolefins are chlorinated compounds obtained by chlorination of polyolefins such as polyethylene. Chlorinated polyolefins are commonly used as modifiers for ABS resins or polyvinyl chloride resins or as wire sheaths, but in recent years they are also coming into wide use as thermoplastic elastomers.

Because of the oil resistance, solvent resistance, weather resistance and flexibility characteristic of chlorinated polyolefins, they are also used as hoses or sheets, packings, automobile joint boots and the like, and such uses also require additional properties such as heat resistance, ozone resistance, satisfactory low-temperature rubber elasticity, compression set and fatigue strength.

[0003]

Chlorinated polyolefins have conventionally been produced by chlorinating polyolefin powder in aqueous suspension while controlling the reaction temperature, chlorine content, etc.

However, the properties of polyolefin powder particles, such as density, differ between the centers and outsides of the particles. Conventional chlorinated polyolefins are therefore considered to have non-uniform chlorine distributions due to this non-uniformity of the polyolefin powder, and satisfactory low-temperature

rubber elasticity has not been achievable.

[0004]

A production method known as a solution to this problem comprises a first step of chlorination at a temperature lower than the crystalline melting point of the polyolefin starting material, a second step of heat treatment in the absence of chlorine at a temperature higher than the crystalline melting point, and a third step of chlorination up to the final chlorine content at a temperature below the temperature of the second step and below the crystalline melting point (see, for example, Patent Document 1).

However, chlorinated polyolefins produced by this conventional method have been unsatisfactory particularly from the standpoint of low-temperature rubber elasticity, compressive set and fatigue strength.

[0005]

[Patent Document 1]

Japanese Examined Patent Publication No. 3-66325  
(pp.1-4)

[0006]

[Problems to be Solved by the Invention]

It is therefore an object of the present invention to provide chlorinated polyolefins with excellent low-temperature rubber elasticity, compression set and fatigue strength, and a process for their production.

[0007]

[Means for Solving the Invention]

As a result of much diligent research directed toward solving the aforementioned problems, the present inventors have completed the present invention based on the discovery that these problems can be overcome by employing a production process wherein pulverized polyolefin powder having a mean particle size of no greater than 500  $\mu\text{m}$  is used as the starting material for chlorination. In other words, the invention relates to chlorinated polyolefins and a process for their

production as specified by the following (1) to (10).

[0008]

(1) A process for production of a chlorinated polyolefin characterized by comprising a step of dissolving and kneading a polyolefin and then molding it into pellets, a step of pulverizing the pellets into powder having a mean particle size of no greater than 500  $\mu\text{m}$ , and a step of chlorinating the powder.

(2) A process for production of a chlorinated polyolefin according to (1) above, wherein the chlorinating step further comprises a first step of chlorination at above the crystalline melting initiation temperature and more than 10°C below the crystal melting peak temperature of the polyolefin starting material as determined by DSC, a second step of interrupting the chlorine supply and performing heat treatment by heating to a temperature which is higher than 5°C below the crystalline melting peak temperature, and a third step of rechlorination at a temperature above the crystalline melting initiation temperature of the chlorinated polyolefin after the heat treatment step.

(3) A process for production of a chlorinated polyolefin according to (1) or (2) above, wherein the density of the polyolefin is 0.91-0.93.

(4) A process for production of a chlorinated polyolefin according to any one of (1) to (3) above, wherein the polyolefin is polyethylene.

(5) A process for production of a chlorinated polyolefin according to (4) above, wherein the polyolefin is polyethylene with a weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) ratio ( $M_w/M_n$ ) of no greater than 3.0 as measured by gel permeation chromatography.

[0009]

(6) A process for production of a chlorinated polyolefin according to (5) above, wherein the polyethylene is linear low-density polyethylene.

(7) A chlorinated polyolefin produced by a process according to any one of (1) to (6) above, wherein the chlorinated polyolefin has a crystal heat of fusion of no greater than 30 J/g according to DSC.

(8) A chlorinated polyolefin according to (7) above, wherein the chlorine content is 15-45 wt%.

(9) A chlorinated polyolefin according to (7) or (8) above, wherein the elongation of the chlorinated polyolefin based on a tensile test is 1500% or greater, and the glass transition point is no higher than -25°C.

(10) A chlorinated polyolefin according to any one of (7) to (9) above, wherein the chlorinated polyolefin is chlorinated polyethylene.

[0010]

[Modes for Carrying Out the Invention]

The chlorinated polyolefin production process of the invention is characterized by comprising a step of melting and kneading a polyolefin and then molding it into pellets, a step of pulverizing the pellets into powder having a mean particle size of no greater than 500 µm, and a step of chlorinating the powder.

Specifically, it is a production process for chlorinated polyolefins which is characterized by melting and kneading polyolefin powder or pellets, and then molding this into pellets which are then pulverized to a mean particle size of no greater than 500 µm to prepare a powder starting material. Here, the mean particle size is represented as the 50% particle size based on weight. A polyolefin starting material with a mean particle size of greater than 500 µm exhibits poor low-temperature rubber elasticity when used for the invention.

[0011]

The step of melting and kneading the polyolefin starting material and molding it into pellets is usually carried out using an extruder or the like, but there are no particular restrictions on the method so long as the

raw material powder obtained from the polyolefin production process is melted and subjected to a step of physical shearing followed by cooling to hardness to achieve the desired homogeneity of the molding material.

[0012]

The pulverization of the obtained pellets is not particularly restricted, although a shearing-type pulverizer is more suitable for pulverization of polyolefins than an impact-type pulverizer, and there are essentially no particular restrictions on the method or type of pulverizer used so long as the mean particle size after pulverization is no greater than 500  $\mu\text{m}$ .

[0013]

As examples of polyolefins to be used for the invention there may be mentioned  $\alpha$ -olefin homopolymers of ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1, 4-methylpentene-1 and the like, and copolymers of ethylene and  $\alpha$ -olefin or copolymers of 2 or more different  $\alpha$ -olefins which are crystalline polymers. Copolymers include random and block copolymers. Two or more of such polyolefins may also be used in combination.

[0014]

The polyolefin preferably has a density of 0.91-0.93. The polyolefin is also preferably linear low-density polyethylene. The polyolefin is preferably polyethylene, and more preferably polyethylene having a weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) ratio ( $M_w/M_n$ ) of no greater than 3.0 as measured by gel permeation chromatography. The  $M_w/M_n$  ratio is preferably between 1.6 and 2.8, and especially between 1.8 and 2.5. If the  $M_w/M_n$  ratio is less than 1.6 the workability may be reduced, and if it exceeds 3.0 the mechanical strength may be reduced.

[0015]

As examples of polyolefins satisfying the conditions described above there may be mentioned those obtained by

polymerization using a metallocene catalyst comprising a metallocene compound of a transition metal selected from Group IVB of the Periodic Table, and an organic aluminoxy compound. As examples of transition metals selected from Group IVB of the Periodic Table there may be mentioned zirconium, titanium, hafnium and the like. As examples of organic aluminoxy compounds there may be mentioned conventional publicly known aluminoxanes obtained by reaction conducted by adding an organic aluminum compound such as trialkylaluminum to a compound containing water of adsorption or a salt containing water of crystallization, for example, aluminum sulfate hydrate or magnesium chloride hydrate suspended in an aromatic hydrocarbon solvent, although there is no restriction to such compounds.

[0016]

The step of chlorination of the powder preferably comprises a first step of chlorination at above the crystalline melting initiation temperature and more than 10°C below the crystal melting peak temperature of the polyolefin starting material as determined by DSC, a second step of interrupting the chlorine supply and performing heat treatment by heating to a temperature which is higher than 5°C below the crystalline melting peak temperature, and a third step of rechlorination at a temperature above the crystalline melting initiation temperature of the chlorinated polyolefin after the heat treatment step.

The chlorination step is preferably conducted so that the final chlorine content in the first step is no greater than 90%.

[0017]

The chlorinated polyolefin obtained by the production process of the invention preferably has a crystal heat of fusion of no greater than 30 J/g according to DSC, because the low-temperature rubber elasticity may be impaired when the heat of fusion

according to DSC exceeds 30 J/g.

The DSC is a method of measurement using a differential scanning calorimeter (JIS K7121 and K7122).

[0018]

The chlorine content of the obtained chlorinated polyolefin is preferably 15-45 wt% and more preferably 20-35 wt%. If the chlorine content is less than 15 wt% or above 45 wt%, the low-temperature rubber elasticity may be impaired.

Also, the elongation of the chlorinated polyolefin based on a tensile test is preferably 1500% or greater, and the glass transition point is preferably no higher than -25°C.

[0019]

[Examples]

The present invention will now be explained in greater detail through examples and comparative examples, with the understanding that the invention is in no way limited by these examples.

The mean particle size was determined by measuring the filtered weight fraction by the Ro-Tap method using a wire sieve according to JIS Z8801, and recording the mean particle size as the particle size with a 50% cumulative weight percentage.

The tensile strength and elongation were measured according to JIS K6301. The Tg was measured according to the method described in Kobunshi Jikkengaku [Polymer Experiments] Vol.12, "Thermodynamic, electrical and optical properties" (Kyoritsu Publishing Co., Ltd.), p.74-77.

[0020]

(Example 1)

Pellets of polyethylene NF-364A (density: 0.920, Mw/Mn: 2.0) by JPO Co., Ltd. were pulverized to a mean particle size of 0.45 mm using a turbogrinder by Turbo Kogyo Co., Ltd.

Next, 80 L of water, 80 g of sodium

alkyldiphenylethersulfonate as a dispersing agent and 80 g of sodium polystyrenesulfonate as an anti-agglomerating agent were added to a 100 L autoclave, and 10 kg of the aforementioned pulverized polyethylene was loaded therein.

The first stage of chlorination was carried out to a chlorine content of 15 wt% at 105°C. The chlorine gas supply was then interrupted, heating to 127°C was followed by cooling to 110°C, and a second stage of chlorination was carried out to a chlorine content of 28 wt% at a temperature of 110°C. The chlorination was followed by water washing and drying by ordinary procedures to obtain chlorinated polyethylene.

[0021]

A test piece was prepared by adding 2 parts by weight of dioctyltin malate and 1 part by weight of calcium stearate as stabilizers to 100 parts by weight of the chlorinated polyethylene, kneading the mixture for 5 minutes with a Brabender kneader at 130°C and then press molding a test piece at a temperature of 170°C and a pressure of 200 kg/cm<sup>2</sup>.

[0022]

(Examples 2-5)

Chlorination was carried out using the starting materials shown in Table 1, and the obtained chlorinated polyethylene was used to fabricate a test piece in the same manner as Example 1.

[0023]

(Comparative Example 1)

Chlorination was carried out in the same manner as Example 1 except that polyethylene powder with a mean particle size of 400 µm was used as the starting material without pulverization, and the obtained chlorinated polyethylene was used to fabricate a test piece in the same manner as Example 1.

[0024]

(Comparative Example 2)

Chlorination was carried out using the starting materials shown in Table 1, and the obtained chlorinated polyethylene was used to fabricate a test piece in the same manner as Example 1.

[0025]

[Table 1]

	Starting material properties				Properties of chlorinated product	
	Form before pulverization	Density g/cm <sup>3</sup>	Mw/Mn	Mean particle size μm	Crystal heat of fusion J/g	Degree of chlorination
Example 1	pellets	0.920	2.0	450	10	28
Example 2	pellets	0.920	2.0	420	1.0	28
Example 3	pellets	0.920	2.0	100	10	28
Example 4	pellets	0.920	2.0	100	1.0	28
Example 5	pellets	0.920	4.0	400	1.0	28
Comp. Ex. 1	powder	0.920	2.0	400	1.0	28
Comp. Ex. 2	pellets	0.920	2.0	800	1.0	28

[0026]

The test pieces obtained by the method described above were used for measurement of tensile strength, elongation and Tg. The results are shown in Table 2.

[0027]

[Table 2]

	Properties of chlorinated product				Gehman test		Compre- ssion set 25% comp CS%
	M100 MPa	Tb Mpa	Elongation %	Tg °C	T2 tempera- ture °C	Freez- ing point °C	
Example 1	1.20	6.06	≥ 1600	-25	-28	-62	29
Example 2	1.05	4.97	≥ 1600	-26	-32	-64	24
Example 3	1.04	3.62	≥ 1600	-25	-28	-62	29
Example 4	0.94	3.42	≥ 1600	-26	-30	-63	25
Example 5	1.20	6.00	≥ 1600	-25	-28	-61	26
Comp. Ex. 1	1.32	8.34	1200	-22	-24	-57	38
Comp. Ex. 2	2.50	10.0	1000	-20	-23	-56	38

[0028]

The chlorinated polyethylene products obtained under the conditions of the examples all had elongation of 1600% or greater in the tensile test and a low 100% modulus, indicating high flexibility. The glass

transition temperatures were also -25°C or below, indicating satisfactory low-temperature flexibility. On the other hand, the chlorinated polyethylene products obtained under the conditions of the comparative examples had poor flexibility and glass transition temperatures exceeding -25°C, indicating poor low-temperature flexibility.

[0029]

The following test was also conducted in order to examine the properties of the crosslinked rubber at low temperature.

To 100 parts by weight of the obtained chlorinated polyethylene there were added 10 parts by weight of magnesium oxide (KYOWAMAG 150-1, product of Kyowa Chemical Industry Co., Ltd.), 50 parts by weight of carbon black (SHOBLACK MAF·G, product of Showa Cabot, KK.) and 40 parts by weight of a plasticizer (SANSOSAIZADOS, product of New Japan Chemical Co., Ltd.), and the mixture was kneaded with a Banbury mixer. After then adding 2.5 parts by weight of 1,3,5-trithiocyanuric acid (TCA-D, product of Ouchishinko Chemical Industrial Co., Ltd.) as a crosslinking accelerator and 1.5 parts by weight of 2-mercaptobenzothiazole (MDCA, product of Ouchishinko Chemical Industrial Co., Ltd.) as a crosslinking agent, the mixture was kneaded with a roll.

For further crosslinking, the kneaded mixture was pressed with a press at 180°C for 6 minutes and heated in an oven at 150°C for 3 hours to obtain a sample.

[0030]

The obtained sample was subjected to a Gehman test (JIS-K6301) and the T2 temperature (temperature at which the rigidity modulus at ordinary temperature doubles) and T5 temperature were compared as the relative modulus.

The crosslinked rubbers of the chlorinated polyethylene obtained under the conditions of the examples had T2 and T5 temperatures of below -25°C and -40°C, respectively, in the Gehman test, indicating high

low-temperature flexibility. Also, the compressive sets were below 30%, indicating a satisfactory balance with low-temperature flexibility.

On the other hand, the crosslinked rubbers of the comparative examples had T2 and T5 temperatures of higher than -25°C and -40°C, respectively, in the Gehman test, indicating poor low-temperature flexibility. Also, the compressive sets were greater than 30%, indicating poor balance with low-temperature flexibility.

[0031]

[Effect of the Invention]

Chlorinated polyethylene obtained by the production process of the invention has excellent flexibility and low-temperature properties, and is therefore useful in the fields of automobiles, household electrical appliances, building materials and the like.